

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-139975

(43)Date of publication of application : 26.05.1998

(51)Int.Cl.

C08L 51/00
C08L101/02
C08L101/04
C08L101/08
// C09D151/00

(21)Application number : 08-302873

(71)Applicant : DAINIPPON INK & CHEM INC

(22)Date of filing : 14.11.1996

(72)Inventor : NAKAMURA HIDEHISA

TANAKA HIROO

(54) RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resin composition which can give coating films having excellent adhesion to polyolefin substrates and good appearance, solvent resistance and abrasion resistance by mixing a graft copolymer obtained by grafting a vinylic monomer mixture onto a chlorinate polyolefin in the presence of an organic solvent with an organometallic compound based curing agent.

SOLUTION: A mixture (B) of a hydroxy vinyl monomer (e.g. 2-hydroxybutyl (meth)acrylate) with a vinylic monomer copolymerizable therewith (e.g. methyl (meth)acrylate) is grafted onto a chlorinated polyolefin (A) exemplified by a chlorinate polyethylene, a chlorinated polypropylene or a chlorinated ethylene/ vinyl acetate copolymer each having a degree of chlorination of about 50% or below in an organic solvent (e.g. toluene or xylene). The ratio of component A to component B is about 10:90 to 90:10 by weight. The obtained graft copolymer having a hydroxyl value of 2-100 is mixed with an organometallic compound based curing agent (e.g. titanium tetrabutylate) to obtain the purpose composition.

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Vinyl system monomer (I) which has a hydroxyl group to chlorinated polyolefins in which a chlorination percentage becomes about 50% or less, a monomeric mixture which consists of this monomer (I) and vinyl system monomer (II) of copolymerizable others -- a weight ratio with said chlorinated polyolefins carried out -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A resin composition making an organic metal system hardening agent (B) blend with a graft copolymer (A-1) which is obtained by making it polymerize under existence of an organic solvent, and which has a hydroxyl value within the limits of 2-100.

[Claim 2] Vinyl system monomer (III) which has an acid radical to chlorinated polyolefins in which a chlorination percentage becomes about 50% or less, a monomeric mixture which consists of this monomer (III) and vinyl system monomer (II) of copolymerizable others -- a weight ratio with said chlorinated polyolefins carried out -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A resin composition making an organic metal system hardening agent (B) blend with a graft copolymer (A-2) which is produced by polymerizing under existence of an organic solvent, and which has acid value within the limits of 2-100.

[Claim 3] A chlorination percentage to chlorinated polyolefins which become about 50% or less Hydroxyl group content vinyl system monomer (I), A monomeric mixture which consists of vinyl system monomer (III) which has an acid radical, and these (I)s, and both monomers as for which (III) becomes and vinyl system monomer (II) of copolymerizable others, a weight ratio with said chlorinated polyolefins carried out -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A resin composition making an organic metal system hardening agent (B) blend with a graft copolymer (A-3) which has the sum total of a hydroxyl value and acid value which are obtained by making it polymerize under existence of an organic solvent within the limits of 2-100.

[Claim 4] Vinyl system monomer (I) which has a hydroxyl group to chlorinated polyolefins in which a chlorination percentage becomes about 50% or less, a monomeric mixture which consists of this monomer (I) and vinyl system monomer (II) of copolymerizable others -- a weight ratio with said chlorinated polyolefins carried out -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A graft copolymer (A-1) which is obtained by making it polymerize under existence of an organic solvent and which has a hydroxyl value within the limits of 2-100, Vinyl system monomer (III) which has an acid radical to chlorinated polyolefins in which a chlorination percentage becomes about 50% or less, a monomeric

mixture which consists of this monomer (III) and vinyl system monomer (II) of copolymerizable others -- a weight ratio with said chlorinated polyolefins carried out -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A resin composition making an organic metal system hardening agent (B) blend with a mixture with a graft copolymer (A-2) which is obtained by making it polymerize under existence of an organic solvent, and which has acid value within the limits of 2-100.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is made new and relates to a useful resin composition. More particularly, this invention relates to the resin composition which comprises in a molecule containing the chlorinated-polyolefins denaturation graft copolymer which has an acid radical and/or a hydroxyl group, and an organic metal system hardening agent as an indispensable constituent, respectively.

[0002] And the place made into the purpose of this invention receives what is called unsettled polyolefin system raw materials, such as a film which should give paintwork and in which various surface treatments do not have ***** in any way, a sheet, or a cast, While it has a function as a primer, it is in providing the resin composition with good adhesion, paint film appearance, solvent resistance, abrasion resistance, etc. which can be painted also by a one coat method and which divides.

[0003]

[Description of the Prior Art] With each, alkyd, an acrylic, or an epoxy resin of a conventional type, etc., with, the formed ^{paint}, As opposed to various mold goods which consist of crystalline polyolefin with small polarity, Do not have ***** adhesion and therefore, the paint to such a polyolefin system substrate, As a primer, using the maleic anhydride denaturation thing of atactic polypropylene or the maleic anhydride denaturation thing of ethylene propylene rubber especially is proposed.

[0004] However, the unsaturated-dicarboxylic-acid denaturation thing of these conventional types, The adhesion over this specific substrate all just by fitness A certain thing, In saying that interlaminar adherability with topcoat is bad, in addition is especially used for one as a clear coating material, When it was said that a coat becomes cloudy or it is applied as enamel which included paints in two, there was the fault or defect of a paint which stability was also missing, from the place of being remarkably inferior to pigment dispersibility.

[0005] Although the method of applying the acrylic resin as an object for topcoats, etc. is also known using chlorinated-polyolefins itself as a primer, Even if it is in such a method, there is a fault that interlaminar adherability with topcoat, solvent resistance, the durable adhesion over a long period of time, etc. fall.

[0006] Although using chlorinated-polyolefins itself as topcoat is also known, it divides, and from the place that hardness, solvent resistance, weatherability, etc. of a coat get remarkably bad, I hear that it is lacking in this and practicality, and it is in them.

[0007] In addition to this, by making urethane resin or an acrylic resin, and an organic metal system cross

linking agent blend with acid modified chlorinated polyolefin resin, respectively, A method etc. which are especially referred to as giving solvent resistance, a water resisting property, etc. are known (for example, JP,5-239292,A).

[0008]However, also from the place that chlorinated polyolefins, and urethane resin or an acrylic resin is the thing comrades of relation lacking in compatibility, it divides and there is a fault of being inferior to stability, paint film appearance, paint stability, etc. of resin.

[0009]

[Problem(s) to be Solved by the Invention]Thus, as long as conventional-type art was followed, it was difficult to obtain the resin composition with very high practicality of excelling also in the adhesion to polyolefin base materials, or surely excelling in paint film appearance, solvent resistance, abrasion resistance, etc. very much.

[0010]

[Means for Solving the Problem]However, the compatibility of chlorinated polyolefins with specific this invention persons, and an acrylic (**) polymer, Further, make it improvement-ize, make adhesion over a polyolefin system substrate, etc. into the start, and, simultaneously with it, further, It divided at the time of considering it as primer specification, and divided at the time of using interlaminar adherability with topcoat, solvent resistance, and topcoat specification, and research was wholeheartedly started so it might also make paint film appearance, solvent resistance, and abrasion resistance nature improve.

[0011]Then, this invention persons aim at Object of the Invention which was mentioned above, Wholeheartedly, as a result of repeating examination, a vinyl system monomeric mixture which uses a hydroxyl group content vinyl system monomer and/or an acid radical content vinyl system monomer as an indispensable raw material component, . Are obtained by saying that a chlorination percentage carries out graft copolymerization to specific chlorinated polyolefins of about 50% or less. A chlorinated-polyolefins denaturation copolymer (denaturation chlorinated polyolefins), Into or a mixture of a chlorinated-polyolefins denaturation copolymer (denaturation chlorinated polyolefins) which has each functional group. A coat which blends and stiffened an organic metal system hardening agent divides, is excellent in paint film appearance, solvent resistance, abrasion resistance, etc., reaches for finding out that adhesion to polyolefins is also good, and it came to complete this invention here.

[0012]Namely, this invention receives fundamentally chlorinated polyolefins in which a chlorination percentage becomes about 50% or less, Respectively A hydroxyl group content vinyl system monomer and/or an acid radical content vinyl system monomer, a monomeric mixture which consists of each of these monomers and a vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, Each which is obtained by making it polymerize under existence of an organic solvent, To a graft copolymer (A-1) which has a hydroxyl value or acid value within the limits of 2-100, or (A-2). Or it is going to provide a resin composition which comprises making an organic metal system hardening agent (B) blend with a graft copolymer (A-3) which has the sum total of a hydroxyl value and acid value within the limits of 2-100,

[0013]In addition, chlorinated polyolefins in which a chlorination percentage becomes about 50% or less are received, a monomeric mixture which consists of a hydroxyl group content vinyl system monomer, and this monomer and a vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, A graft

copolymer (A-1) which is obtained by making it polymerize under existence of an organic solvent and which has a hydroxyl value within the limits of 2-100, A chlorination percentage to chlorinated polyolefins which become about 50% or less An acid radical content vinyl system monomer, a monomeric mixture which consists of this monomer and a vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, It is also going to provide a resin composition which comprises making an organic metal system hardening agent (B) blend with a mixture with a graft copolymer (A-2) which is obtained by making it polymerize under existence of an organic solvent, and which has acid value within the limits of 2-100.

[0014]

[Embodiment of the Invention]Thus, this application receives the chlorinated polyolefins in which a chlorination percentage is set to one about 50% or less, the monomeric mixture which consists of a hydroxyl group content vinyl system monomer, and this monomer and the vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, The resin composition is charged [which comprises making an organic metal system hardening agent (B) blend with the graft copolymer (A-1) which is obtained by making it polymerize under existence of an organic solvent, and which has a hydroxyl value within the limits of 2-100], [0015]As opposed to the chlorinated polyolefins in which a chlorination percentage is set to two about 50% or less, the monomeric mixture which consists of an acid radical content vinyl system monomer, and this monomer and the vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, The resin composition is also charged [which comprises making an organic metal system hardening agent (B) blend with the graft copolymer (A-2) which is obtained by making it polymerize under existence of an organic solvent, and which has acid value within the limits of 2-100], [0016]As opposed to the chlorinated polyolefins in which a chlorination percentage is set to three about 50% or less, Respectively A hydroxyl group content vinyl system monomer and an acid radical content vinyl system monomer, the monomeric mixture which consists of each of these monomers and a vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, The sum total of the hydroxyl value and acid value which are obtained by making it polymerize under existence of an organic solvent is also charging [which comprises making an organic metal system hardening agent (B) blend with the graft copolymer (A-3) which is within the limits of 2-100] the resin composition, [0017]And the chlorinated polyolefins in which a chlorination percentage is set to four about 50% or less are received, the monomeric mixture which consists of a hydroxyl group content vinyl system monomer, and this monomer and the vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, The graft copolymer (A-1) which is obtained by making it polymerize under existence of an organic solvent and which has a hydroxyl value within the limits of 2-100, A chlorination percentage to the chlorinated polyolefins which become about 50% or less An acid radical content vinyl system monomer, the monomeric mixture which consists of this monomer and a vinyl system monomer of copolymerizable others -- a weight ratio with these chlorinated polyolefins -- about 10: -- about 90 - about 90: -- about, as ten becomes comparatively, The resin composition is also charged [which comprises making an organic metal system hardening agent (B) blend with a mixture with the graft

copolymer (A-2) which is obtained by making it polymerize under existence of an organic solvent, and which has acid value within the limits of 2-100].

[0018]Although this invention is made below to explain much more in detail, If the above-mentioned chlorinated polyolefins carry out the designation of the polyolefine which has preferably about 50% or less of the chlorination percentage in 10 to 40% of within the limits and it limits for illustrating only a thing especially typical as this polyolefine first in here, [0019]. As [represent / with ethylene, propylene, 1-butene, or 4-methyl-1-pentene] Homopolymer or copolymer; or the ethylene-vinylacetate copolymer of what is called alpha olefin of the versatility of publicly known common use, It is a copolymer with a vinyl system monomer of the alpha olefin and others of the versatility of publicly known common use which is represented with an ethylene-butadiene copolymer or an ethylene-acrylic ester copolymer, etc.

[0020]If it limits for illustrating only a typical thing especially as the chlorinated polyolefins concerned, . As [represent / with chlorinated polyethylene, chlorinated polypropylene, chlorination ethylene propylene rubber, or a chlorination ethylene-vinylacetate copolymer] It is what is called acid modified chlorinated polyolefin resin etc. of the versatility of publicly known common use of the form which is a maleic anhydride of what is called various chlorinated polyolefins or each of those copolymers of publicly known common use, and these various copolymers, etc., with was processed.

[0021]In here, about the chlorination percentage of the chlorinated polyolefins concerned, In saying that this chlorination percentage becomes too much high exceeding about 50%, Neither of the cases is never preferred also from the place that the adhesion over a polyolefin system substrate, etc. fall easily, and the solubility to the organic solvent of chlorinated polyolefins, etc. surely fall easily in, saying that this chlorination percentage is less than about 10% on the other hand.

[0022]In consideration of various coat performances, such as such division, adhesion, stability, flexibility, and hardness, it should succeed in the determination of this chlorination percentage, and it is desirable, 10 to 40% of within the limits is still more preferred, and 15 to 35% of within the limits is suitable for it.

[0023]typical [especially as said hydroxyl group content vinyl system monomer (I) carried out] in this invention -- so-called -- it limits for illustrating, if it becomes, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-hydroxypropyl (meta) acrylate, 2-hydroxybutyl (meta) acrylate, 3-hydroxybutyl (meta) acrylate, 4-hydroxybutyl (meta) acrylate, Hydroxymethylcyclohexylmethyl (meta) acrylate, 3-chloro-2-hydroxypropyl (meta) acrylate, What is called various unsaturated double bond content mono- or dicarboxylic acid of publicly known common use which is represented with di-2-hydroxyethyl fumarate or mono-2-hydroxyethyl monobutyl fumarate, It is the so-called resultant with dihydric alcohol of the versatility of publicly known common use, etc., and is an adduct of each of these unsaturated double bond content mono- or a dicarboxylic acid-monohydric alcohol resultant, and epsilon-caprolactone, etc. further.

[0024]subsequently, if it limits for illustrating only a typical thing especially as said acid radical content vinyl system monomer (III) carried out, they will be a maleic anhydride, fumaric acid, itaconic acid, citraconic acid, or (meta-) acrylic acid.

[0025]supra -- if the bottom limits for illustrating only a typical thing especially as vinyl system monomer [like] (II) of others respectively as copolymerizable as hydroxyl group content vinyl system monomer (I) and/or acid radical content vinyl system monomer (III) [0026]Methyl (meta) acrylate, ethyl (meta) acrylate, n-propyl (meta) acrylate, Iso(i)-propyl (meta) acrylate, n-butyl (meta) acrylate, i-butyl (meta) acrylate, tert-

butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, [0027]Cyclohexyl (meta) acrylate, 4-tert-butyl-cyclohexyl (meta) acrylate, Various kinds of acrylate (meta) like benzyl (meta) acrylate, dibromopropyl (meta) acrylate, tribromophenyl (meta) acrylate or alkoxy alkyl (meta) acrylate, and ISOBO nil methacrylate;

[0028]Various kinds of unsaturated dicarboxylic acid [like / maleic acid, fumaric acid, or itaconic acid], Diester with monohydric alcohol; vinyl acetate, benzoic acid vinyl, or "BEOBA" (the product made by Netherlands SHIERU) Various kinds of vinyl ester like the trade name of vinyl ester; "the screw coat 8F, 8FM, 17FM, 3F, or 3FM" [trade name of a fluorine-containing acrylic monomer made from Osaka Organic chemistry], [0029]Like perfluoro cyclohexyl (meta) acrylate, JIPA fluorocyclohexyl fumarate, or N-i-propyl perfluoro octane SURUHONAMIDOECHIRU (meta) acrylate, What is called a fluorine-containing compound of the versatility of publicly known common use of various kinds of fluoro (par) alkyl group content which is represented with - vinyl ester, - vinyl ether, - (meta) acrylate, or - unsaturated carboxylic acid ester, respectively;

[0030]Or (meta) acrylonitrile etc. are begun and they are what is called olefins of the versatility of publicly known common use which is represented with VCM/PVC, vinylidene chloride, and vinyl fluoridation, vinylidene fluoride, etc. further.

[0031]For the purpose of a coat dividing and raising weatherability etc. further. For example, it can also carry out as copolymerization of the ultraviolet ray absorbent of what is called polymerization nature of the versatility of publicly known common use which is represented with "T-37", "LA-82" [ADEKAAGASU Chemicals products], etc., the SadamuMitsuyasu-ized agent, etc. is carried out.

[0032]It faces preparing a graft copolymer (A-1), (A-2), (A-3), or a graft copolymer (A-4) from various monomers which have been hung up above, respectively, The amount of hydroxyl group content vinyl system monomer (I) and/or acid radical content vinyl system monomer (III) used, In the single use of each reactant polar group (functional group) content vinyl system monomer. Are concomitant use, with, in about 2 - about 100 within the limits, a hydroxyl value, acid value, or the sum total of a hydroxyl value and acid value, respectively preferably, What is necessary is just to carry out as the graft polymerization reaction of this monomer (I) and/or (III), and vinyl system monomer (II) of copolymerizable others is mixed and carried out so that it may become within the limits of 5-50.

[0033]In here, when [these] a hydroxyl value, acid value, or the sum total of a hydroxyl value and acid value says that it is less than two, respectively, Bridge construction hardenability becomes scarce easily, and if it pulls, surely, In a coat's dividing, and solvent resistance, abrasion resistance, etc. becoming easy to be inferior and, saying that it becomes too much high exceeding about 100 on the other hand, surely dividing -- the adhesion to polyolefin base materials -- since the adhesion to a polypropylene substrate, etc. are easily inferior above all, neither of the cases is preferred.

[0034]various monomers (mixture) which have been hung up above are polymerized to the chlorinated polyolefins mentioned above -- making, if it hits, these -- respectively -- as the use rate of chlorinated polyolefins and this monomer (mixture) -- the former chlorination thing:latter -- a monomer (mixture) -- a weight section ratio -- with, about 10: -- about 90 - about 90: -- within the limits of 15:85-60:40 is [about 10 within the limits] suitable preferably.

[0035]By such a polymerization reaction, for example, acrylic ester (meta) etc. Although what is called denaturation chlorinated polyolefins of the form where what is called a vinyl system monomer component

of the versatility of publicly known common use was graft-ized by the chlorinated-polyolefins ingredient, and good compatibility was given as a result are obtained, [0036]as the method of such a polymerization reaction -- usually -- the polymerization temperature of about 60-100 ** -- with, Although it is appropriate to carry out solution polymerization using what is called a radical generating nature polymerization initiator of the versatility of publicly known common use which is represented with benzoyl peroxide or azobisisobutyronitrile and it is appropriate to depend on a solution radical polymerization above all, [0037] as [mentioned / above / in this case] -- respectively -- the ratio of chlorinated polyolefins and a monomer (mixture) -- a weight section ratio -- with, surely, when the quantity of chlorinated polyolefins decreases too much exceeding 10:90, Since the adhesion over a polyolefin system substrate, etc. fall easily, it is not desirable, and since the solvent resistance etc. of the coat obtained surely fall easily remarkably on the other hand when the quantity of chlorinated polyolefins increases too much exceeding 90:10, it can come, ** and is not desirable.

[0038]Although it is known as a good solvent to chlorinated polyolefins as solution polymerization which was mentioned above, and an organic solvent for performing a solution radical polymerization above all, for example, various solvents of publicly known common use of toluene or xylene are mentioned in here, It can also be said that it chooses suitably and uses within within the limits which does not deviate from the purpose of this invention within limits in which solvents, such as butyl acetate and butanol, do not spoil ** and solubility besides these, either, or limits which do not spoil the effect of this invention.

[0039]it is obtained as mentioned above -- respectively -- a graft copolymer (A-1), (A-2), or (A-3) -- or -- a graft copolymer (A-4) -- various kinds of copolymers, First, about 5,000 - about 40,000 within the limits are preferred, and the number average molecular weight (Mn) is suitable for within the limits of 8,000-30,000.

[0040]Case [like the thing of a molecular weight lower than about 5,000], It divides and is never enough in respect of a mechanical strength etc., and since it divides and spray workability etc. surely come to fall in, saying that it is higher than about 40,000 on the other hand, neither of the cases is preferred.

[0041]If it limits for illustrating only a typical thing especially as the above mentioned organic metal system hardening agent which is the (B) ingredient in this invention, so-called alcoholate with the polyvalent metal of the versatility of publicly known common use which is represented with aluminum, titanium, a zirconium, etc., etc. will be begun, [0042][of publicly known common use which is represented with acetic acid or propionic acid / what is called various organic acid and supra] -- the bottom -- salt [with various polyvalent metal / like];, or supra -- the bottom is chelate compound of various polyvalent metal [like], etc.

[0043]If it limits for illustrating only such an especially typical thing as chelate compound of alcoholate; organic acid-polyvalent-metallic-salt [with polyvalent metal];, or polyvalent metal, respectively, What is called aluminum alcoholate of the versatility of publicly known common use which is represented with aluminum ethylate, aluminum propionate, or aluminum butyrate;

[0044]An aluminum bis(ethyl acetate)monoiso PUROPI rate, aluminum-triethyl aceto acetonate, aluminum bis(ethylacetooacetate)monoacetyl acetonate or aluminum -- doria -- what is called aluminum chelate compound; of the versatility of publicly known common use which is represented with cetyl acetonate etc.

[0045]Titanium alcoholate, such as titanium ethylate, titanium propionate, and titanium butyrate; A CHITANTORI (ethyl acetate) monoiso PUROPI rate, What is called titanium chelate compound of the versatility of publicly known common use which is represented with titanium tetra ethyl acetoacetonate, titanium bis(ethylacetooacetate)diacetyl acetonate, or titanium tetra acetylacetone;

[0046]Or zirconium alcoholate, such as zirconium ethylate, zirconium propionate, and zirconium butyrate; A JIRUKONIUMUTORI (ethyl acetate) monoiso PUROPI rate, It is what is called zirconium chelate compound etc. of the versatility of publicly known common use which is represented with zirconium tetra ethyl acetoacetone, zirconium bis(ethylacetacetate)diacetyl acetonate, or zirconium tetra acetylacetone.

[0047]Subsequently, as amount of the organic metal hardening agent used concerned, It is a rate which exists in the target resin composition and which becomes [within the limits of about 0.5-2 Eq] within the limits of 0.8-1.2 Eq preferably to 1 Eq of a carboxy group and/or a hydroxyl group, respectively, and you are such a rate, with what is necessary is just to make it blend.

[0048]In a coat's dividing to the case below about 0.5 Eq, and solvent resistance's etc. being surely easily inferior to it and, saying that it increases too much exceeding about 1.5 Eq on the other hand, Since a coat divides and weatherability, a water resisting property, etc. fall easily, neither of the cases is never preferred.

[0049]I hear that the resin composition concerning this invention divides addition of an ultraviolet ray absorbent etc., and it makes endurance etc. improvement-ize further further, and there is. Therefore, what is necessary is just to carry out suitably, each time if needed, as you make it choose, add and mix.

[0050]If it limits for illustrating only a typical thing especially as the ultraviolet ray absorbent concerned, Benzophenone, 2,4-dihydrobenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2'-dihydroxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone, 2-hydroxy-4-methoxy-5-sulfonylbenzophenone, 5-chloro-2-hydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxy-5-sulfonylbenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone, 2-hydroxy-4-(2-hydroxy-3-methylacryloxy isopropoxy benzophenone);

[0051]2-(2'-hydroxy-5'-methyl-phenyl)-Benzotriazol, 2-(2-hydroxy-3,5-di-tert-amyl phenyl)-2H-benzotriazol, 2-(2'-hydroxy-3',5'-di-tert-butyl-phenyl) benzotriazol, 2-(2'-hydroxy-3',5'-di-tert-butyl-5'-methyl-phenyl) benzotriazol, 2-(2'-hydroxy-3',5'-di-tert-butyl-phenyl)-5-chloro-benzotriazol, 2-(2'-hydroxy-3',5'-di-tert-isoamyl phenyl) benzotriazol, (2-hydroxy-5-tert-butylphenyl) Benzotriazol, phenyl salicylate 4-tert-butyl-phenyl salicylate, p-octyl-phenyl salicylate;

[0052]Ethyl-2-cyano 3,3'-diphenyl-acrylate, 2-ethylhexyl 2-cyano 3,3'-diphenyl-acrylate; A hydroxy-5-methoxy-acetophenone, 2-hydroxy-naphthophenone; -- 2-ethoxyethyl p-octyl methoxycinnamate; -- nickel screw OKUCHIRUFENIRUSURU Fayd; -- 4-benzoyloxy 2, 2, and 6 and 6-tetramethylpiperidine. It is bis-(2, 2, 6, and 6-tetramethyl 4-piperidyl)sebacate or the "tinuvin 292" (Ciba-Geigy products), and, as for these, it is needless to say that single use or two or more sorts of concomitant use may be sufficient.

[0053]"Sumi Reiser BHT" since still much more validity is increased [Sumitomo Chemical Co., Ltd. products], "SHINOKKUSU BCS [Shiroishi Calcium products]", "IRUGA NOx 1010 or 1076" (Switzerland Ciba-Geigy products), ****, such as "NOKURAIZA TNP" [Ochi New products] or "antioxidant KB" (Germany Beyer company products), and various antioxidants of publicly known common use can be used together.

[0054]The resin composition concerning this invention obtained in this way, the adhesion over a long period of time, or interlaminar adherability with topcoat -- as if -- giving [of saying that it excels in the adhesion in a large meaning, etc., and also a coat dividing, and excelling in solvent resistance etc.] a cured film with many very valuable coat performances [0055]Therefore, the resin composition concerning

this invention receives various kinds of various polyolefin system raw material or substrates like mold goods including a film, a sheet, etc., It can use broadly, and can apply, for example, may use as a primer in the paint to a polyolefin molding, [0056]or it may use as topcoat to various structures or structures -- it carries out, and it uses as a binder for printer's ink further, and applies, although it can also carry out, It is especially very useful as a paint for various kinds of casts made from polyolefine, a structure, or structures, etc.

[0057]As opposed to the polyolefin molding of the form where what is called bulking agents of the versatility of publicly known common use which is especially represented with calcium carbonate, talc, or silica were blended, It is the form which it tells that the outstanding adhesion etc. are shown and with which various additive components of publicly known common use of the paints as a clear coating material, a leveling agent, etc. were combined, with, of course, may be used as enamel.

[0058]

[Example]Next, although this invention is made to explain much more concretely according to a reference example, an example, and a comparative example, this invention is never limited only to these examples of illustration. Unless a notice has a part and % especially in below, it shall be a weight reference altogether.

[0059]Reference example 1 [The example of preparation of a graft copolymer slack chlorinated-polyolefins denaturation copolymer (A)]

[0060]500 copies of "HADOREN 14-ML [trade name; chlorination percentage =26% by Oriental Chemical Industry of chlorinated polypropylene and solid content =30%]" and 800 copies of toluene were put into the reaction vessel equipped with the agitator and the condensator, and temperature up of the degree of vessel internal temperature was carried out even to 80 **.

[0061]There Subsequently, 520 copies of methyl methacrylate (MMA), 300 copies of methacrylic acid isobutyl (i-BMA), and 30 copies of methacrylic acid (MAA), The melted object in which n-butanol of 350 copies was made to dissolve five copies of benzoyl peroxide (BPO) and five copies of azobisisobutyronitrile (azobisisobutironitoriru) was carried out under ** for 3 hours.

[0062]The chlorinated polypropylene denaturation acrylic resin in which in the appropriate back solid content acid value is [a nonvolatile matter] 20 at 40.2%, and a number average molecular weight becomes the ** 20,000 by saying that it holds for 12 hours was obtained.

[0063]Each, a polymerization solvent, an initiator as shown in the reference example 2 - the 8 1st table, Various kinds of chlorinated-polyolefins denaturation acrylic copolymers were obtained like the reference example 1 except having changed so that a polymerization nature unsaturated bond content monomer and chlorinated polyolefins might be used, and having changed so that it might be polymerization conditions as shown in the table, with might moreover carry out.

[0064]

[Table 1]

第 1 表 (1-1)	参考例 2	参考例 3
「ハードレン 14-ML」 「ハードレン 14-LLB」 トルエン n-ブタノール	1, 300	1, 700 110
MMA i-BMA CHMA スチレン MAA β -HEMA	300 450 50	410 20 60
BPO AIBN	4 6	10
n-ブタノール	167	200

[0065]<<Footnote of the 1st table>> Each of each numbers of preparations in a table shall be the numbers of weight sections.

[0066]"HADOREN 14-LLB" Trade name; chlorination percentage =26% by Oriental Chemical Industry of chlorinated polypropylene, and solid content =15% [0067]Beta-HEMA.....The brief sketch of methacrylic acid beta-hydroxyethyl or beta-hydroxyethyl methacrylate (an alias is also called methacrylic acid 2-hydroxyethyl or 2-hydroxyethyl methacrylate.) [0068]

[Table 2]

第 1 表 (1-2)	参考例 2	参考例 3
不揮発分 (%)	40.3	40.9
Mn 固体分酸価 固体分水酸基価	18,000 20	25,000 13 25

[0069]

[Table 3]

<u>第 1 表 (2-1)</u>	参考例4	参考例5
「ハードレン 14-ML」	5 0 0	6 6 7
「ハードレン 14-LLB」	2 0 0	
トルエン	8 3 0	7 3 3
MMA	2 0 0	5 0 0
i-BMA	1 9 8	
CHMA	1 5 0	1 4 5
スチレン	2 0 0	
MAA	7 2	
β -HEMA		2 5 5
BPO	7	6
AIBN	2	4
n-ブタノール	1 5 0	2 0 0

[0070]

[Table 4]

<u>第 1 表 (2-2)</u>	参考例4	参考例5
不揮発分 (%)	40. 9	40. 2
Mn	24, 000	26, 000
固体分酸価	47	
固体分水酸基価		110

[0071]

[Table 5]

<u>第 1 表 (3-1)</u>	参考例 6	参考例 7
「ハードレン 14-ML」 「ハードレン 14-LLB」 トルエン	1, 0 0 0 6 0 0	3, 0 5 0
MMA	2 9 8	5 5
i-BMA	2 0 0	
CHMA		
スチレン	2 0 0	
MAA	2	3 0
β -HEMA		
BPO	4	2
AIBN	5	1
n-ブタノール	2 0 0	1 9 8

[0072]

[Table 6]

<u>第 1 表 (3-2)</u>	参考例 6	参考例 7
不揮発分 (%)	4 0. 1	3 0. 2
Mn	1 8, 0 0 0	2 1, 0 0 0
固体分酸価	1. 3	2 0
固体分水酸基価		

[0073]

[Table 7]

第 1 表 (4-1)	参考例 8
「ハードレン 14-ML」	
「ハードレン 14-LLB」	600
トルエン	890
MMA	500
i-BMA	60
CHMA	300
スチレン	
MAA	
β -HEMA	50
BPO	6
AIBN	6
n-ブタノール	100

[0074]

[Table 8]

第 1 表 (4-2)	参考例 8
不揮発分 (%)	40.6
Mn	23,000
固体分酸価	
固体分水酸基価	20

[0075] 158 copies of the graft copolymer obtained by the example 1 reference example 1, 35 copies of titanium oxide, and 35 copies of xylene were made to mill for 1 hour by a sand mill, and object slack and coating resin composition slack white enamel were acquired.

[0076] Subsequently, add two copies of titanium tetra butyrate to this white enamel, and are thinner which becomes toluene / xylene / n-butyl acetate = 1/1 / 1 (weight section ratio), with it dilutes even to spray viscosity, After making it paint on a polypropylene (PP) board, at 70 **, baking during 30 minutes was performed and the appropriate back neglected it for one week to the room temperature.

[0077] About the cured film obtained in this way, the evaluation judging of many of these coat performances was performed. The result of those evaluation judgings is summarized and is shown in the 2nd table.

[0078] Except having changed so that it might be considered as a blending ratio as shown in Examples 2-5 and the comparative example 1 - the 4 2nd table, like Example 1, various kinds of white enamel was prepared, the hardening agent was added, and henceforth produced various kinds of cured films like Example 1. Henceforth performed the evaluation judging of many coat performances about each cured film like ** and Example 1. The result of those evaluation judgings is summarized and is shown in the 2nd

table.

[0079]

[Table 9]

第 2 表 (1)		実施例 1	実施例 2	実施例 3
練 肉 配 合 比	参考例 1 の樹脂 参考例 2 の樹脂 参考例 3 の樹脂 酸化チタン キシレン	1 5 8 3 5 3 5	1 5 5 3 5 4 0	1 5 0 3 4 3 8
硬 化 剤 類	チタンテトラブチレート ジルコニウムトライセチルアセトネート アルミニウムトリスアセチルアセトネート	2	3	3
塗 膜 諸 性 能	光沢値	8 0	8 2	8 1
	PP 付着性	良 好	良 好	良 好
	耐溶剤性	良 好	良 好	良 好
	耐摩耗性	良 好	良 好	良 好

[0080]<<Footnote of the 2nd table>> Each of each numbers of preparations in a table shall be the numbers of weight sections.

[0081][The evaluation judging method of many coat performances]

[0082]PP adhesion It is for carrying out the evaluation judging of the adhesion to a polypropylene (PP) substrate, and, therefore, a 2-mm width cross cut test requires. That is, the above examinations were carried out after making it immersed for ten days into 40 ** warm water.

[0083]Solvent resistance 1 kg of load was applied on the felt impregnated with gasoline, it is this felt, with the appearance of the painted surface after grinding a cured film 20 times was judged by viewing.

[0084]Abrasion resistance The appearance of the painted surface after grinding a cured film 30 times with the rubber containing sand under 1 kg of load was judged by viewing.

[0085]

[Table 10]

第 2 表 (2)		実施例4	実施例5	比較例1
練 内 配 合 比	参考例4の樹脂 参考例2の樹脂 参考例5の樹脂 酸化チタン キシレン	1 5 0 3 5 3 7	7 5 7 9 3 5 4 0	1 5 0 3 9 4 5
硬 化 剤 類	ジルコニウムテトラアセチル アセトネート アルミニウムトリスアセチル アセトネート チタンテトラアセチルアセト ネート	5	4. 5	1 3
塗 膜 諸 性 能	光沢値	8 2	8 1	8 0
	PP付着性	良 好	良 好	劣 る
	耐溶剤性	良 好	良 好	良 好
	耐摩耗性	良 好	良 好	良 好

[0086]

[Table 11]

第 2 表 (3)		比較例 2	比較例 3	比較例 4
練 内 配 合 比	参考例 6 の樹脂 参考例 7 の樹脂 参考例 8 の樹脂 酸化チタン キシレン	1 6 0 3 5 3 7	2 1 7 3 5 1 0	1 5 5 3 5 2 0
硬 化 剤 類	ジルコニウムテトラアセチル アセトネート アルミニウムトリスアセチル アセトネート チタンテトラアセチルアセト ネート	0. 2	2. 4	2. 7
塗 膜 諸 性 能	光沢値	8 0	7 0	8 2
	PP 付着性	良 好	良 好	劣 る
	耐溶剤性	劣 る	劣 る	良 好
	耐摩耗性	劣 る	劣 る	良 好

[0087]As explained in full detail above, the resin composition concerning this invention, It is reasonable that it is a thing [say / excelling in coating operability, paint appearance, etc., in addition especially excelling in the adhesion to unsettled polyolefin base materials, solvent resistance, abrasion resistance, etc.] which has very high practicality, and it can know.

[0088]

[Effect of the Invention]Thus, the resin composition concerning this invention is a thing [say / dividing, and excelling in coating operability, paint appearance, etc., in addition excelling in the adhesion to unsettled polyolefin base materials, solvent resistance etc., and excelling in abrasion resistance etc. further] which has very high practicality.

[Translation done.]